# THE ROLE OF MOLECULAR DIFFUSION IN THE ADHESION

# OF ELASTOMERS


by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Butyl rubber (polyisobutylene-co-isoprene) mixed with polyisobutylene was crosslinked to yield elastomeric macromolecular networks containing dissolved linear macromolecules. Adhesion of these materials to themselves (self-adhesion) and to an inert substrate was investigated over a wide range of peel rates and test temperatures. Greatly enhanced self-adhesion was found when linear polyisobutylene molecules of

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high molecular weight were present, but the strength of adhesion to a rigid inert substrate was hardly affected. The enhancement of self-adhesion is attributed to interdiffusion of polyiso-butylene molecules. It was greatest at intermediate peel rates and temperatures, becoming insignificant at extremely low rates, probably because the diffusing species can then migrate readily, and at high effective rates of peel when the polymer approaches the glassy state and the strength of adhesion is high in all cases. A transition to somewhat lower levels of adhesion at relatively high rates of peel is tentatively ascribed to the onset of molecular fracture in place of pull-out. The presence of large amounts of low-molecular-weight polyisobutylene ($M_v$ = 50,000 g/mole) increased the level of self-adhesion and of adhesion to an inert substrate to a similar degree, over a broad range of peel rates. This effect is attributed primarily to enhanced viscous losses in the elastomeric layer during separation. Application of these results to crack and weld-line healing in, glassy plastics is discussed.

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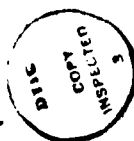
1. Introduction

Diffusion of polymer molecules across an interface has been proposed to play a major role in adhesion (1,2). Certainly the development of self-adhesion or "tack" between two layers of materials seems likely to involve the diffusion of molecules across the interface after the layers have been brought into intimate contact (3-9). Even here, however, the question is not decided. The development of intimate contact is, itself, a relatively slow process and could be the rate-determining step in self-adhesion (10). Indeed, molecular interdiffusion may not be required at all; molecular contact may be sufficient for strong adhesion between layers of the same, or even of different polymers (11, 12).

In an attempt to separate the effects of intimate contact from those of molecular interdiffusion, studies have now been carried out of the adhesion of a simple model system, consisting of a crosslinked elastomer layer containing a proportion of uncrosslinked linear macromolecules. In this system, the crosslinked macromolecules are unable to diffuse readily but at least for low degrees of crosslinking they are able to conform to small surface irregularities and make molecular contact (13, 14). The dissolved linear molecules are presumably able to diffuse readily across an interface into any compatible material. Thus, by comparing the adhesion of crosslinked layers with and without linear molecules present, the contribution from molecular interdiffusion can be elucidated.

The system employed consists of butyl rubber, a co-polymer of isobutylene and isoprene containing only 1.6 per cent of isoprene and hence wholly compatible with linear polyisobutylene, in admixture with various amounts of poly-isobutylene of various molecular weights. The butyl rubber fraction could be crosslinked by reaction of the isoprene groups with conventional difunctional sulfurating reagents, leaving the polyisobutylene molecules dissolved in an elasto-meric matrix.

The viscoelastic properties of such systems, containing a linear polymeric species within a gelled matrix, have been described by Ferry and co-workers (15, 16). Measurement of adhesion for such materials is not a simple matter, however. The work of separating one layer of an elastomer from another, or from a rigid substrate, depends strongly upon the rate of propagation of the line of separation and upon the test temperature (17-20). It is clear that the mechanical strength of an adhesive joint depends upon both the intrinsic strength of the interface and upon the viscoelastic properties of the adhering materials (21, 22). Thus, in order to clarify the role of interdiffused molecules upon the strength of adhesion, it has proved necessary to study the response over a wide range of test speeds and temperatures.

## 2. Experimental details

### (a) Materials

Mixtures of butyl rubber (IIR) and polyisobutylene were prepared on an open two-roll mill using Butyl 301 (Polysar Ltd., Canada), which has a viscosity-average molecular weight $\overline{M}_V$ of $4 \times 10^5$ g/mole and 1.6 mole per cent of unsaturation, and one of three grades of polyisobutylene (Vistanex, Exxon Chemical Company): LM-MH, denoted L5 here, with $\overline{M}_V$ of $5 \times 10^4$ g/mole; MML-100, denoted L100 here, with $\overline{M}_V$ of $1.1 \times 10^6$ g/mole; and MML-140, denoted L140 here, with $\overline{M}_V$ of $1.8 \times 10^6$ g/mole. Various proportions of polyisobutylene were added, up to 100 per cent of the butyl rubber content, or 50 per cent of the total.

Preliminary studies were carried out to find a vulcanization recipe that yielded crosslinked sheets essentially free from "bloom", i.e., surface contamination by additives or by-products of the vulcanization reaction. Reasonable success was achieved with the following recipe, in parts by weight: Butyl 301, 100; polyisobutylene, 0 to 100; zinc oxide, 5; tetramethylthiuram disulfide, 5; zinc-2-ethyl hexanoate, 2. Crosslinking was effected by heating for 3 to 4 h at $148^{\circ}$C in a heated press.

Sheets about 1.5 mm thick were prepared in this way with one surface adhering to a thin cotton cloth backing and the other molded against a polished Ferrotype plate to yield a smooth glossy surface.

Since polyisobutylene is fully saturated it should not
participate in the crosslinking reaction.    Crosslinked sheets
                                            or carbon tetrachloride
were extracted for long periods with boiling hexane ^in order
to assess the ease with which the polyisobutylene could be
removed from the crosslinked material.    Although extraction was
extremely slow, after four weeks 85 to 95 per cent of L5 poly-
isobutylene and 80 to 95 per cent of L100 had been extracted,
indicating that the polyisobutylene was, indeed, substantially
independent of the butyl rubber molecular network.

(b)  Measurement of self-adhesion

Preliminary experiments were carried out to find optimum
contact conditions so that no further increase in strength
could be obtained with higher contact pressures.    It was found
sufficient to place test strips in contact for 14 h at a temper-
ature of 60$^{\circ}$C under a pressure of about 1 MPa.    These conditions
gave reasonably reproducible results and were therefore adopted
in all cases.

Strips, about 15 mm wide and 150 mm long, were pressed
together and then separated in a T-peel geometry, Figure 1.
The cloth backing served to minimize extension of the separated
parts under the action of the peel-force $\underline{F}$.    Under these
circumstances, the work $G_a$ of separation per unit area of
interface is given by

$$G_a = 2F/w \tag{1}$$

where $\underline{w}$ is the width of the adhering strips.    Results are
given below in terms of $G_a$ for comparison with other measurements

of adhesion, and also for comparison with the work $G_c$ required to propagate a tear through unit area of the same material.

(c) <u>Adhesion to a rigid substrate</u>

Measurements were also made of the adhesion of test strips to a rigid inert substrate. For this purpose, sheets of polyethylene terephthalate (Mylar 300 A, E.I. du Pont de Nemours and Co.) were glued flat to a steel plate. Test strips were pressed into close contact and then peeled back at an angle of $180°$, Figure 1b. Again, the work $G_a$ of separation is given by equation 1.

(d) <u>Fracture energy</u>

Values of the work $G_c$ required to propagate a tear through unit area were determined by cutting through the cloth backing of a test strip with a sharp knife and then measuring the tear force $F$, Figure 1c. Equation 1 yields values for $G_c$ in this case when $w$ is replaced by the thickness $t$ of the rubber layer, assuming that the tear path is, indeed, perpendicular to the plane of the layer.

Measurements were also made of $G_c$ for uncrosslinked materials. Samples of the polymers were milled to an equivalent degree to that required for mixing in the vulcanization ingredients and then pressed between two layers of thin cotton cloth to form a sandwich about 1.5 mm thick. Test strips were cut from such sheets, about 20 mm wide and 150 mm long. The cloth backing on both sides was then cut through along the center line leaving the thickness of the polymer layer to be torn through, as in Figure 1c.

## 3. Results and discussion

### (a) Adhesion to Mylar

Experimentally-determined values of the work $G_a$ of separation of test strips from a Mylar substrate are plotted in Figure 2 against the rate $R$ of advance of the line of separation.   In view of the wide range employed for $R$, and the large variation in the strength of adhesion $G_a$ at various rates and temperatures, logarithmic scales have been used for both axes.   Each point represents an average of the measured peel force over a peel distance of about 100 mm, averaged for at least three test strips.

At the highest temperature employed, 100°C, and at the lowest rate of peel, 4 $\mu$m/s, the value obtained for $G_a$ was extremely low, only about 1-2 J/m$^2$.   On the other hand, at the lowest temperature, -20°C, and at the highest peel rate, about 10 mm/s, the value obtained for $G_a$ was relatively high, about 1 kJ/m$^2$, and detachment took place in a stick-slip fashion with the peel force oscillating between high and low values.

This marked dependence of $G_a$ upon peel rate and temperature is reminiscent of other viscoelastic processes.   Indeed, when the results shown in Figure 2 are replotted against the reduced rate of peel $Ra_T$ appropriate to ambient temperature, 25°C, then they are all found to fall on a single curve, Figure 3. This successful superposition of results over a wide tempera-ture range shows that the temperature dependence of $G_a$ arises

solely from rheological effects within the elastomer
itself, associated with the motion of molecular segments, and
not with variations in its wetting properties, or surface
attractions.   Similar results have been obtained previously
for the adhesion of simple pressure-sensitive adhesives (19,23)
and for the adhesive and fracture properties of other elasto-
mers (20,24,25).

In the present instance, values of $a_T$ were calculated
from  the relation given by Ferry as appropriate for poly-
isobutylene (26),

$$\ln\ a_{T_g} = -38(T - T_g)/(104 + T - T_g) \qquad (2)$$

where $T$ denotes the test temperature and $T_g$ the glass transition
temperature of polyisobutylene, $203^{\circ}K$.   It should be noted
that the second numerical coefficient in equation 2 is
considerably different from the "universal" value of $52^{\circ}C$,
reflecting the well-known relatively-sluggish response of
polyisobutylene at temperatures well above its glass trans-
tion temperature. The results shown in Figures 2 and 3 are
for a sample containing 20 parts (16.7 per cent of the total
amount of polymer) of L100 polyisobutylene.   Similar results
were obtained for a control sample containing no polyisobutylene,
and for samples containing up to 100 parts (50 per cent of the
total) of L100, Figure 4.   There is a significant increase in
the work of separation in the latter case but the effect is
comparatively small.   Thus, the presence of uncrosslinked
polymer of high molecular weight does not appear to increase

the strength of adhesion much to an inert substrate. In contrast, as shown later, the strength of self-adhesion is greatly enhanced.

(b) <u>Self-adhesion of a control sample</u>

Adhesion to itself of a butyl rubber sample containing no polyisobutylene was studied over the same wide ranges of test temperature and peel rate. Again, the results at different temperatures were found to superimpose satisfactorily by plotting them against the effective rate of peel $Ra_T$ at ambient temperature, the factor $a_T$ being calculated for each test temperature by means of equation 2. The results are shown in Figure 5, together with a broken curve representing the strength of adhesion of the control sample to a Mylar substrate.

At all effective rates of peel the strength of self-adhesion is seen to be somewhat greater then the strength of adhesion to Mylar, by a factor of about 3 at most. This enhanced adhesion is probably due largely to a greater affinity between butyl rubber and itself than between butyl rubber and a Mylar substrate, but it may also reflect some interdiffusion of molecular segments across the interface. The crosslinked polymer was found to contain a relatively large soluble fraction, about 20 per cent, and the network itself will have long pendant molecular chains attached to it only at one end, that can interdiffuse to a limited extent.

(c) <u>Self-adhesion of samples containing high-molecular-</u>
       <u>weight polyisobutylene</u>

When the two layers pressed into contact contained high-molecular-weight polyisobutylene, then the strength of

adhesion was found to be sustantially  higher than before.

Some representative results are shown in Figure 6.   Now,

however, use of the WLF reduction factor $a_T$, calculated by

means of equation 2, was less successful in superimposing

experimental results obtained at different temperatures onto

a single curve in terms of a reduced rate of peel $Ra_T$.

Instead, as shown in Figure 6, the results appeared to fall

on two overlapping curves, so that a broad but discontinuous

transition occurred at relatively high effective rates of

peel (or equivalently at low temperatures) to lower strengths.

This transition occurred over 3-4 decades of reduced peel

rate, approaching

the glass transition region, and amounted at most to a drop by 50 per cent in the measured strength. Nevertheless, it was observed consistently in systems where the strength is mainly associated with interdiffused and entangled molecules, as noted later. It is therefore tentatively attributed to a particular feature of such systems: that the interconnecting molecules can either disentangle or break. The former process will become increasingly difficult as the peel rate is increased, so that at some critical rate, depending upon the molecular weight of the interlinking molecules and their speed of diffusion, they will break instead of disentangling.

Some reduction in peel strength can well occur when the mechanism of detachment changes, even when the interfacial stresses continue to rise. This is because the peel force represents the _work_ expended in detachment, and does not necessarily follow the detachment stress for strongly non-linear systems (20). For example, a marked reduction in peel force is found at the transition from liquidlike flow to rubberlike elasticity in soft viscoelastic adhesives (20). Thus, if the _work_ expended in breaking interdiffused molecules is less than that required to disentangle them, then the observed peel force would be expected to decrease at the transition from one mode of failure to the other.

Further discussion of the observed transition in strength of self-adhesion for samples containing polyisobutylene is deferred until later. The principal effect of the presence of polyisobutylene is to cause a marked increase in the strength of self-adhesion, by a factor of about 5 in comparison with the self-adhesion of a control sample containing no polyisobutylene and by a factor of over 10 in comparison with the adhesion to a Mylar substrate, at rates of peel some-what below the transition, i.e., at peel rates of the order of $100\,\mu$m/s at room temperature (Figure 6). This effect is attributed to the presence of interdiffused linear polyisobuty-lene molecules spanning the interface. At lower effective rates of peel the effect becomes relatively small, presumably because the linear molecules can then diffuse readily back again. At higher effective rates of peel, in the vicinity of the glass transition, the enhancement of self-adhesion is again relatively small, probably because then the interdiffused molecules are broken rather than disentangled and they contribute less to the total work of separation.

In Figure 7 the strength of self-adhesion at an inter-mediate rate of peel, $400\,\mu$m/s, is plotted against the amount of polyisobutylene incorporated. Addition of more than 15-20 per cent does not appear to cause any further increase in the level of self-adhesion. It seems likely that the density of interlinking molecules at the interface does not increase significantly with a further increase in their concentration in the two contacting layers (27).

(d) <u>Effect of low-molecular-weight polyisobutylene</u> ($\overline{M}_v = 50,000$ g/mole

Experimental results for the strength of ▬ adhesion to Mylar
of a butyl rubber compound containing 17 and 50 per cent of
the low-molecular-weight polyisobutylene L5 (LM-MH) are shown in
Figure 8.   Corresponding relations for the strength of self-
adhesion ▬ are represented by broken curves in Figure
8.   For each sample the strength of self-adhesion is quite
similar to the strength of adhesion to Mylar at all effective
rates  of peel.   However, the addition of 50 per cent of
L5 causes a substantial increase in adhesion whereas addition
of 17 per cent has little effect, giving results similar to
those obtained for a control sample containing no polyiso-
butylene, Figure 5.

These results are quite different from those obtained
by addition of high-molecular-weight polyisobutylene, described
in the preceding section.   Then, the level of self-adhesion
was increased substantially, at least over a certain range
of effective peel rates, whereas the strength of adhesion
to Mylar was not much affected.   Moreover, additions of 17
to 50 per cent were virtually equivalent.   These effects were
ascribed to interdiffusion of linear macro-molecules at the interface.

In contrast, the present results suggest that diffusion
of low-molecular-weight polyisobutylene molecules across the
interface does not contribute significantly to the strength of
self-adhesion.   Low-molecular-weight species can presumably
diffuse back readily under all circumstances  and they will be

less able to form entanglements with the molecular networks that contain them, so that a major enhancement of strength is less likely in this case as a result of interdiffusion.

The origin of the substantial increase, both in self-adhesion and in adhesion to Mylar, must therefore be sought elsewhere. Ferry et al have shown that the loss compliance $J''$ is greatly increased over a range of effective frequencies of deformation from 1 x $10^{-4}$ rad/s to 10 rad/s, when 50 per cent of L5 is present within a crosslinked butyl rubber (15). Over most of the same frequency range the loss compliance is hardly changed at all by the presence of 50 per cent of a high-molecular-weight polyisobutylene. (It is increased in a similar way only at lower frequencies: 1 x $10^{-3}$ rad/s and below (15).) Now, the effective deformation frequency in a peeling experiment is given approximately by $R/t$, where $R$ is the peel rate and $t$ is the thickness of the elastomer layer. Thus, the range of effective frequencies over which L5 has a major effect on the loss compliance whereas L100 has little effect is equivalent to the range of peel rates; 1 $\mu$m/s to 10 mm/s; over which the principal changes in the strength of adhesion are observed. It is therefore concluded that the enhanced strength of adhesion observed with L5 arises from greater energy losses within the adhering layer as it is deformed in the peeling process. These losses are apparently unimportant with L100 over the same range of peel rates.

(e)   Adhesion of butyl rubber containing polyisobutylene
      to a control sample.

Strips of the butyl rubber compound containing 17 per cent
of L100 polyisobutylene were pressed into contact with strips
of the butyl rubber compound containing no added polyisobuty-
lene.   Measurements of the work    $G_a$   of separation are
plotted in Figure 9 against the effective peel rate $Ra_T$   at
25°C.   The results are seen to be similar, both in form and
magnitude, to those obtained previously for the strength of
self-adhesion of the material with 17 per cent of L100, Figure 6.

As before, the present results show a transition over a
broad range of peel rates.   Indeed, they differ only by a
small factor over the entire range of effective peel rates,
being consistently somewhat lower than the values of self-
adhesion.   Thus, it appears that diffusion of linear polyiso-
butylene molecules takes place across the interface with a butyl
rubber control sample and leads to enhanced adhesion in this
case also.   The somewhat lower values of adhesion may reason-
ably be ascribed to a lower density of interlinking molecules
when they are supplied by only one of the contacting strips.

(f)  <u>Comparison of the work of separation</u> $G_a$ <u>with the</u>
     <u>work of fracture</u> $G_c$.

The work $G_a$ of separating two adhering layers is quite
large in some cases (for example, when linear polyisobutylene
molecules are present) and it approaches the intrinsic strength
of the layers themselves.  Indeed, incipient tearing of the
layers was observed for the strongest bonds.  It is therefore
of interest to compare the work of fracture of the layers with
the work required to separate them.

Measurements were made of the work $G_c$ of fracture per
unit area torn through for the butyl rubber compound containing
17 per cent of linear polyisobutylene L100 and for the L100
polymer itself.  In the latter case there is no permanent
molecular network and therefore, at least at the lowest rate
of "tearing", the molecules presumably disentangle and flow
apart, rather than break.  It is particularly interesting
to note that the measured fracture energy for this material,
when plotted against the effective rate $Ra_T$ of tear propagation,
calculated by means of equation 2 from measurements at various
rates and temperatures, does not fall on a single curve but
shows a diffuse transition to lower values at high effective
rates of tearing, Figure 10.  This behavior  closely resembles
that found for self-adhesion of the butyl rubber compound
containing 17 per cent of L100 polyisobutylene, represented
by the broken curves in Figure 10, and lends support to the
hypothesis that the transition reflects a change from molecular

slippage to molecular rupture.

This hypothesis is further strengthened by the observation that no similar transition is observed in measurements of the work of fracture for the crosslinked butyl rubber containing a small proportion (17 per cent) of linear polyisobutylene. As shown in Figure 11, although the work of fracture for this material is comparable in magnitude to that for the linear polymer alone, and depends in a similar way upon the effective rate of tear propagation, there is no indication of a transition from one level of fracture energy to another (lower) level over a characteristic range of tear rates. Molecular slippage is, of course, prevented in this sample at all rates of deformation by the presence of chemical crosslinks.

(g)    Relaxation times for linear polyisobutylene molecules
          within a butyl rubber network.

An indication of the characteristic relaxation time for linear polyisobutylene molecules within a butyl rubber network may be obtained from the delayed elastic response of the material. Measurements were therefore made of the tensile creep compliance $D(t)$ as a function of time $t$ under load, for butyl rubber compounds containing 50 per cent of each linear polyisobutylene. The results are plotted in Figure 12.

As can be seen in the Figure, the butyl rubber compound containing no added polyisobutylene has a low compliance of about $1 \times 10^{-6}$ $m^2/N$, increasing slowly with time over long periods. In contrast, whereas the material containing

50 per cent of high-molecular-weight linear polyisobutylene
L100 shows a similar low compliance at short times, it then
increases relatively rapidly to reach a value of about
$1 \times 10^{-5}$ $m^2/N$ after times under load of the order of $10^7$ s.
For the material containing 50 per cent of low-molecular
weight linear polyisobutylene L5, the tensile compliance is
large, even after times under load as short as 10 s, and it
appears to reach a quasi-equilibrium value of about
$1 \times 10^{-5}$ $m^2/N$ after about $10^4$ s under load.

The equilibrium levels of the excess compliance shown by
materials containing linear polyisobutylene. can be regarded
as substantially equal. They probably reflect a lower degree
of          crosslinking in diluted butyl rubber. The obvious
differences in response time may be attributed to the different
times taken by linear polyisobutylene molecules of different
molecular weight to rearrange themselves and allow the butyl
rubber network to support the applied load fully. If it is
assumed that the whole response curve is similar in form for
different polyisobutylenes, and merely shifted to shorter or
longer times by a multiplying factor, then the compliance
curves shown in Figure 12 can be superimposed by lateral  shifts
to form a master response curve applicable to all molecular
weights. The curve obtained in this way is shown in Figure 13.

From the shift factors and master curve, the times $t_r$
required for one-half of the excess compliance to be attained
may be estimated for each material. These times are a reasonable

measure of the "reptation" time or relaxation time for each sample of polyisobutylene when embedded within a butyl rubber network. The values obtained are about 0.3 s for L5 and about $3 \times 10^4$ s for L100.

Similar values have been deduced by Ferry et al from dynamic mechanical measurements on the same systems (15). The present values are also in rough accord with their conclusions that the principal relaxation times are proportional to the third power of molecular weight of the entrapped linear species.

We therefore infer that the principal relaxation time for molecules of L100 polyisobutylene within a butyl rubber network is quite long, about 12 h at room temperature. This explains why it was found necessary to press samples together for relatively long periods to achieve an equilibrium level of adhesion.

An estimate of the time allowed for molecular rearrangement during the peeling process may be obtained from the effective rate $e$ of elongation (given approximately by $R/t$, where $R$ is the peel rate and $t$ is the thickness of the rubber layer) and the maximum elongation $e_m$ undergone by the rubber at the point of separation. The total time permitted for molecular rearrangement is then given approximately by $e_m t/R$.

As shown in Figures 6, 9 and 10, the transition in cohesive and adhesive strength for materials containing linear polyisobutylene of high molecular weight occurs over a range of effective rates of peeling and tearing beginning at about

100 $\mu$m/s at 25°C. Thus, the permitted response time is about 100 s, taking the value of $e_m$ to be 5-10 and putting t = 1.5 mm. This is considerably shorter than the relaxation time of the polyisobutylene molecules within a butyl rubber matrix, estimated above to be about $3 \times 10^4$s. However, only about one-half of an interlinking molecule, at most, is required to disentangle in order to permit separation. Indeed, on average, relaxation of about one-fourth of the length of "tie" molecules will be sufficient. Assuming an $M^3$ relationship between molecular length (weight) and relaxation time, a time of about 500 s is therefore estimated to be required, for substantial disentanglement of molecules crossing an interface. This is comparable to, although somewhat larger than, the time permitted for molecular rearrangement during peeling or tearing at the critical rate. Thus, the onset of the transition in peel strength and tear strength is reasonably consistent with the time scale of relaxation processes for dissolved polyisobutylene molecules.

(h) **Kinetics of adhesion**

The effect of contact time upon the strength of self-adhesion and adhesion to Mylar is shown in Figure 14 for a crosslinked sample of butyl rubber containing 50 per cent of L100 polyisobutylene. These measurements were made at a peel rate of 400 $\mu$m/s and at a temperature of 25°C, when the relative difference between the two strengths is greatest (see Figure 6).

As shown in Figure 14, the strength of self-adhesion does not reach a constant value until after periods of contact of the order of $10^5$ s at 25°C. This time period is similar to the mean relaxation time $t_r$ of the linear macromolecules present, deduced from studies of creep compliance (section g), and is thus consistent with the hypothesis that the rate-controlling process in self-adhesion is the interdiffusion of linear polyisobutylene molecules.

An estimate of the mean distance $\left(\overline{x^2}\right)^{\frac{1}{2}}$ that a molecule can diffuse through within the relaxation time $t_r$, or within the similar time required to attain the maximum level of self-adhesion, can be deduced from the Einstein equation:

$$\overline{x^2} = 2Dt_r. \tag{3}$$

A value for the diffusion coefficient $\underline{D}$ is readily obtained from the measured steady-state flow viscosity $\underline{\eta}$ of polyisobutylene L100 ($\underline{\eta}$ = 2 x $10^8$ Ns/m$^2$ at 25°C), using Bueche's relation (28):

$$D \eta = \rho RT(\overline{r^2}/M)/36$$

where the density $\rho$ is approximately $1 \times 10^6$ g/m$^3$, the characteristic ratio $\overline{r^2}/M$ is approximately $6 \times 10^{-21}$ m$^2$ mole/g and $R$ and $T$ denote the gas constant and the absolute temperature, respectively. In this way, an estimate for $D$ is obtained of $2 \times 10^{-21}$ m$^2$/s at 25$^o$C, yielding a value for $(\overline{x^2})^{\frac{1}{2}}$ of about 10 nm when a value for $t_r$ of $3 \times 10^4$s is employed in equation 3. Thus, the mean distance through which a molecule can diffuse within the characteristic relaxation time $t_r$, or within the similar time of contact required to reach the maximum level of self-adhesion, is of the same order as the size of the random-coil molecule itself. It seems quite reasonable that interdiffusion to this extent would give a fully-developed bond.

(i)    Implications for crack and weld-line "healing"

When glassy polymers are brought together and annealed, they soften and come into closer contact.   If they are compatible, then a process of molecular interdiffusion will take place as in the experiments described here for layers of butyl rubber.   The strength of adhesion of joints prepared in this way, measured after cooling them back to the glassy state, has been attributed largely to molecular inter-diffusion (5, 6, 8, 9), although quite strong joints are formed between incompatible materials as well (12).

The present experiments show that the level of adhesion for viscoelastic materials can be quite high, even in the absence of molecular interdiffusion.   Indeed, a clear contrib-ution from interdiffused molecules can only be recognized over a limited range of rates of separation and temperature, and then only for diffusing species of relatively high molecular weight.   Under the $_\wedge^{se}$ circumstances the strength of adhesion may be increased by a factor of 10 or more as a result of interdiffusion.   This increase appears to be due in part to the additional work required to disentangle interlinking molecules.   When the rate of separation is too high , then the molecules appear to break,rather than flow,and their contribution to the observed strength is reduced.

Similar experiments on polymers in the glassy state seem necessary in order to establish the magnitude of the contribu-tion of interdiffused molecules to the strength of adhesion in that case also, and to separate it from contributions due solely to adsorption.

## Conclusions

The following general conclusions are obtained:

1. The strength of adhesion of lightly-crosslinked butyl rubber to itself and to a rigid (Mylar) substrate is greatly dependent upon the rate of peeling detachment and upon the test temperature, increasing by more than three orders of magnitude. as the peel rate is increased and the test temperature is reduced. The effect of test temperature is in good accord with the Williams, Landel and Ferry relation for molecular segmental mobility in simple viscoelastic substrates.

2. Addition of high-molecular-weight linear polyisobutylene to lightly-crosslinked butyl rubber leads to enhanced self-adhesion, but to little change in the strength of adhesion to Mylar. The enhancement is attributed to interdiffusion of polyisobutylene molecules between the contacting layers. · It reaches a maximum value of about 10X at intermediate rates of peel, being smaller both at

    low rates when back diffusion is relatively rapid, and at high rates, approaching the glass transition, when the strength of adhesion is high in all cases.

3. A small but significant decrease in strength of adhesion, and of the fracture energy of polyisobutylene, starting at a peel rate or tear rate of about $100 \mu m/s$ at $25^\circ C$, is attributed to a change from flow to fracture of the inter-linking molecules when the rate of elongation is too

rapid to permit them to disentangle and separate.

4.  Addition of small amounts of a low-molecular-weight
    polyisobutylene does not significantly enhance the
    strength of self-adhesion or adhesion to a Mylar substrate.
    At higher concentrations both are increased strongly, by a
    factor of about 10X. This effect is attributed to
    enhanced viscous energy losses within the elastomer layer.
    Interdiffusion does not appear to increase the strength
    of adhesion significantly, in this case.

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## Figure Legends

Figure 1. Methods of measurement (a) Self-adhesion

(b) Adhesion to Mylar

(c) Fracture energy

Figure 2. Effect of peel rate $\underline{R}$ and test temperature $\underline{T}$ upon the adhesion to Mylar of a sample containing 17% L100.

Figure 3. Data from Figure 2 plotted against the effective peel rate $\underline{Ra_T}$ at a temperature of 25$^\circ$C. Values of $a_T$ were calculated for each test temperature from equation 2.

Figure 4. Work $\underline{G_a}$ of detachment from Mylar of a butyl rubber compound containing 50 per cent L100, plotted against the effective peel rate $\underline{Ra_T}$ at 25$^\circ$C. The broken curve denotes the response of compounds containing 0 and 17 per cent L100.

Figure 5. Work $\underline{G_a}$ of separation of a sample containing no polyisobutylene from itself (full curve) and from Mylar (broken curve) ~~taken from Figure 3~~ , plotted against the effective peel rate $\underline{Ra_T}$ at 25$^\circ$C.

Figure 6. Work $\underline{G_a}$ of separation for self-adhering strips of a sample containing 17 per cent L100, plotted against the effective peel rate $\underline{Ra_T}$ at 25$^\circ$C. The broken curve represents the self-adhesion of a sample containing no polyisobutylene, taken from Figure 5, and the lower curve represents the adhesion to Mylar, taken from Figure 3.

Figure 7.  Work $G_a$ of separation for self-adhering strips
of samples containing various amounts of L100
and L140.   Peel rate: 400 $\mu$m/s.   Test temperature:
$25^oC$.

Figure 8.  Work $G_a$ of separation from Mylar of samples cont-
aining 17 per cent and 50 per cent of L5 (LM-MH),
plotted against the effective peel rate $Ra_T$ at
$25^oC$.   The broken curves represent the work of
separation for self-adhering strips of the same
materials.

Figure 9.  Work $G_a$ of separation for a butyl rubber compound
containing 17 per cent of L100 adhering to a butyl
rubber compound containing no polyisobutylene,
plotted against the effective peel rate $Ra_T$ at $25^oC$.
The broken curves represent the self-adhesion of the
material containing 17 per cent L100.

Figure 10.  Work $G_c$ of fracture for polyisobutylene L100 plotted
against the effective rate $Ra_T$ of tear propagation
at $25^oC$.   The broken curves represent the self-
adhesion of a butyl rubber compound containing 17
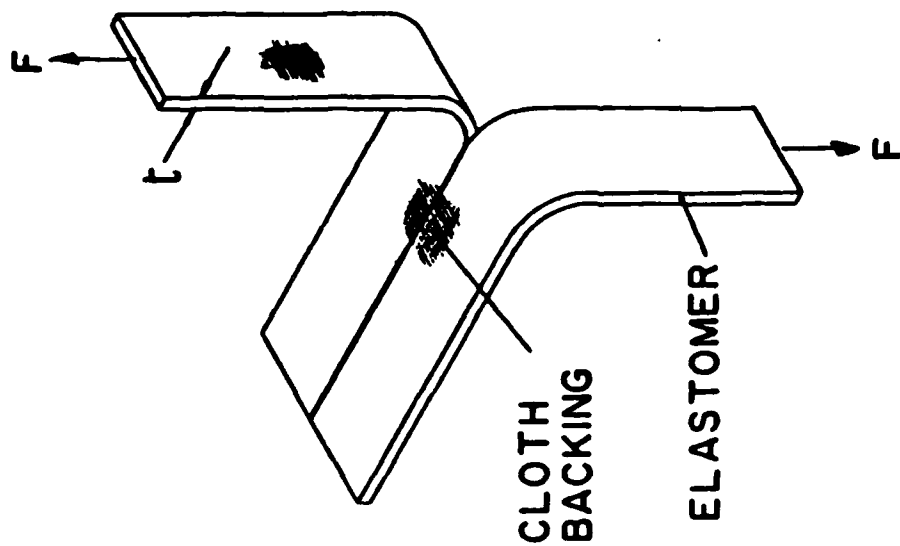per cent L100 (taken from Figure 6).

Figure 11.  Work $G_c$ of fracture at $25^oC$ for a butyl rubber
compound containing 17 per cent of linear polyiso-
butylene L100.   The broken curves represent the work
of fracture for the L100 polymer alone, taken from
Figure 10.

Figure 12. Tensile creep compliance $\underline{D(t)}$ plotted against time $\underline{t}$ under load for butyl rubber compounds containing 50 per cent of L5 polyisobutylene, 50 per cent of L100 polyisobutylene, and no polyisobutylene.
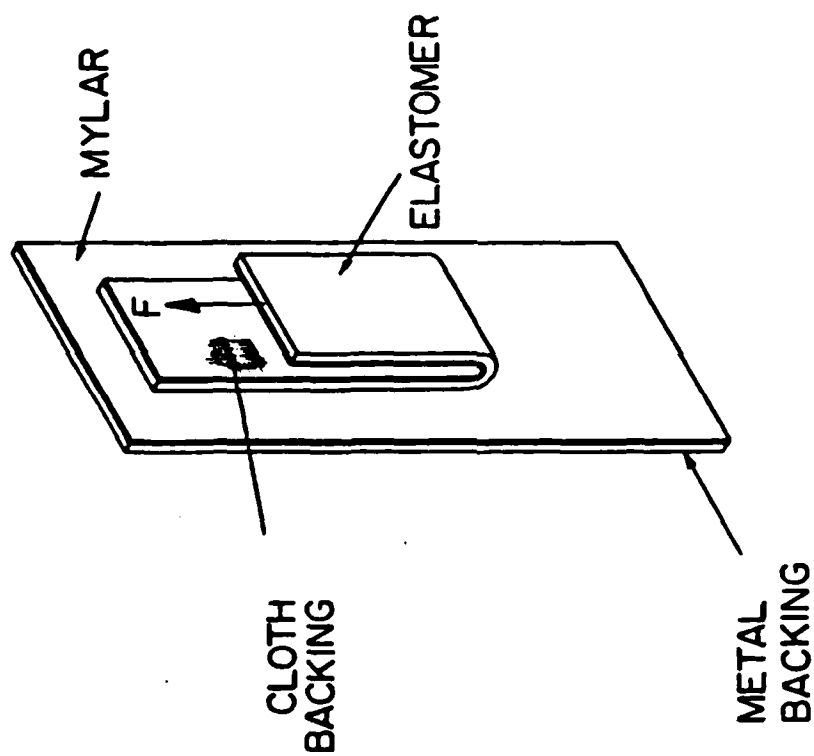
Figure 13. Tensile creep compliance $\underline{D(t)}$ plotted against the effective time $\mathbf{t}\,\underline{\mathbf{a}_M}$ under load at $25^{\circ}C$. Butyl rubber with L5 polyisobutylene (50/50), $\square$, $\underline{\mathbf{a}_M = 1 \times 10^5}$; butyl rubber with L100 polyiso-butylene (50/50), $\triangle$, $\blacktriangle$, $\underline{\mathbf{a}_M = 1}$.

Figure 14. Work $\underline{G_a}$ of separation plotted against time of contact for a butyl rubber compound containing 50 per cent of L100 polyisobutylene. Peel rate: $400\,\mu m/s$.

(a)

(b)

(c)

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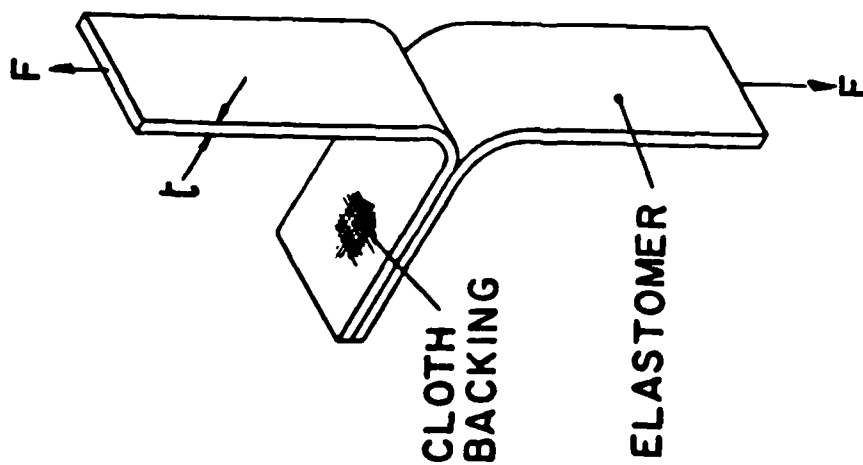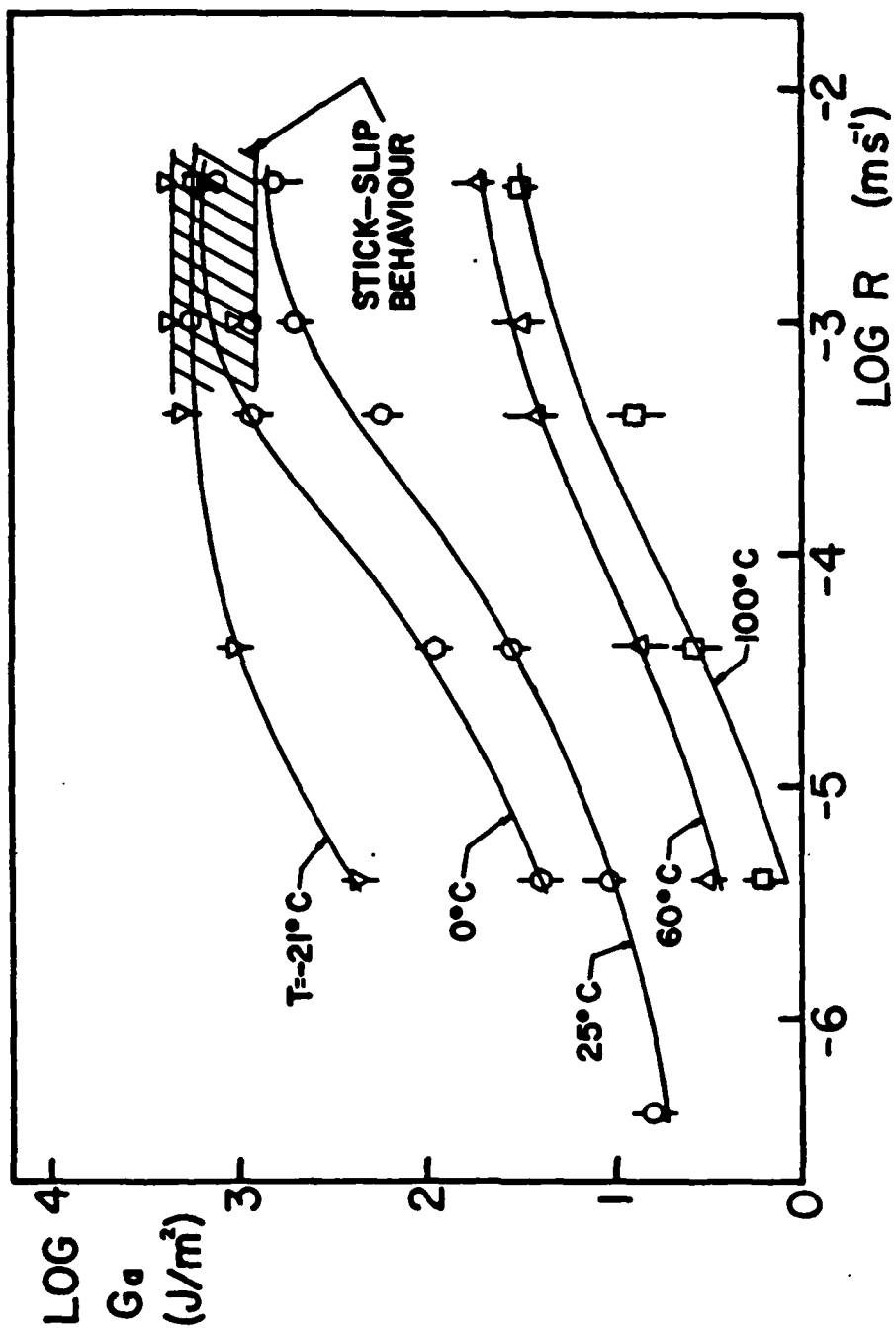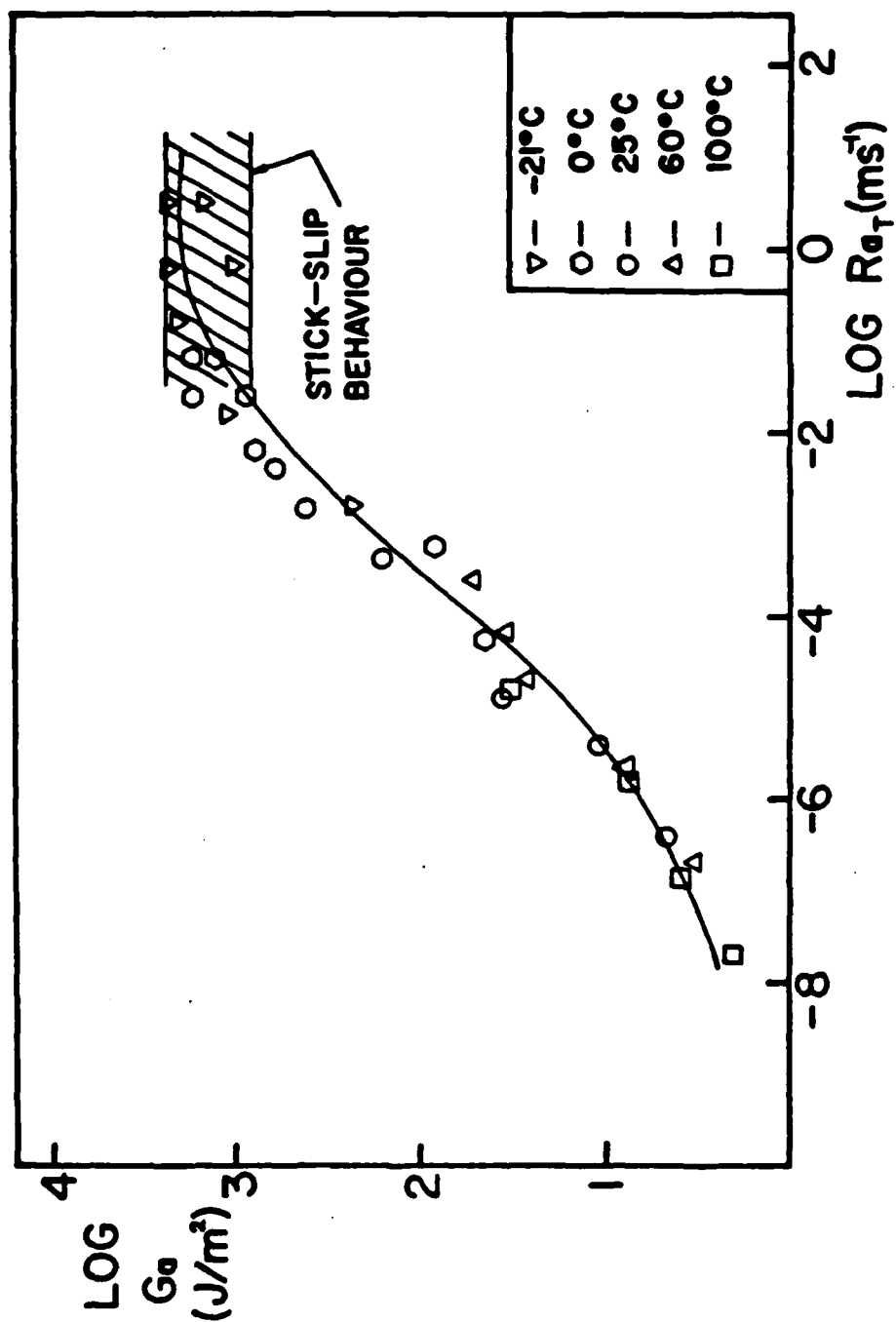CLOTH BACKING

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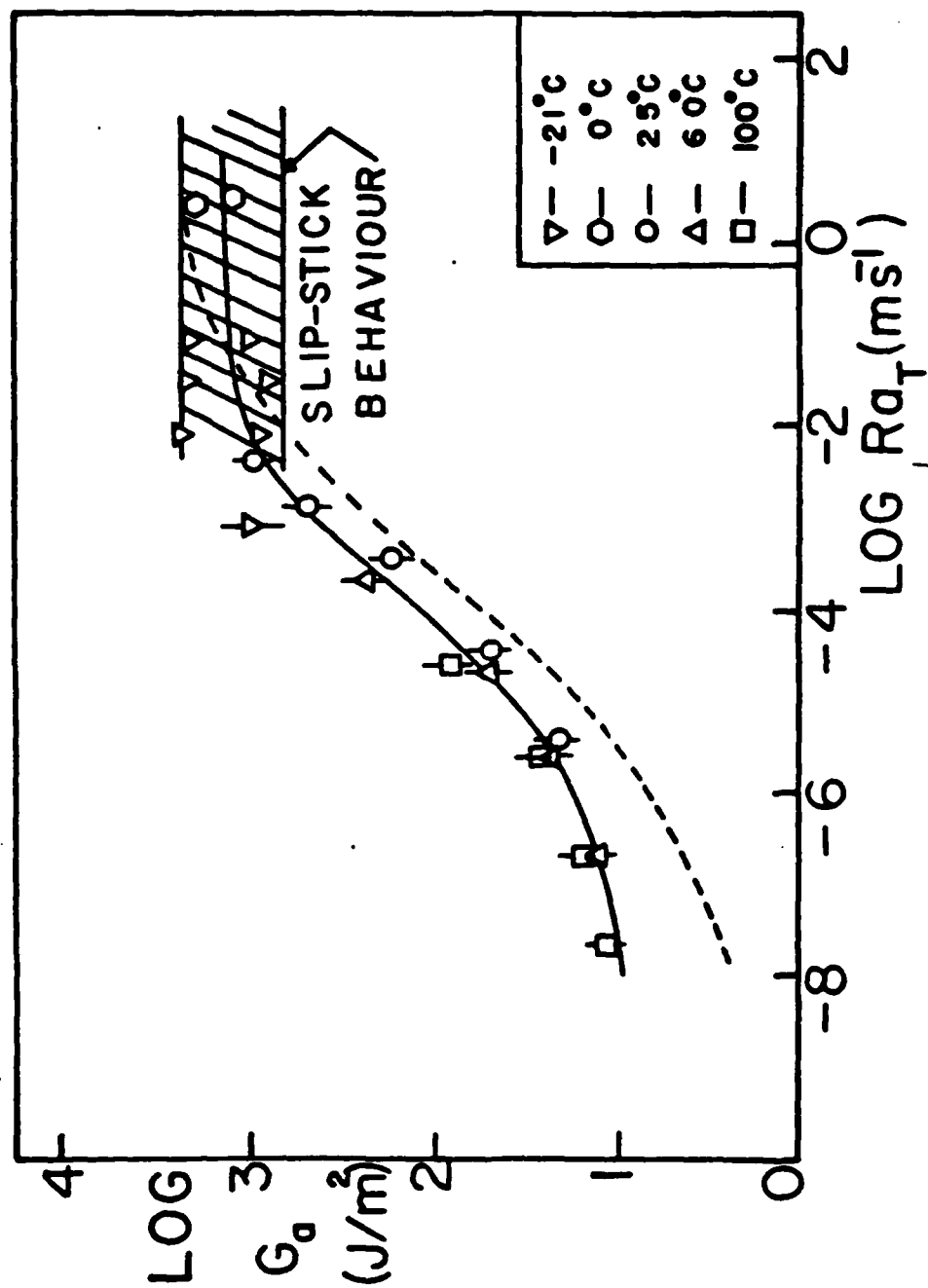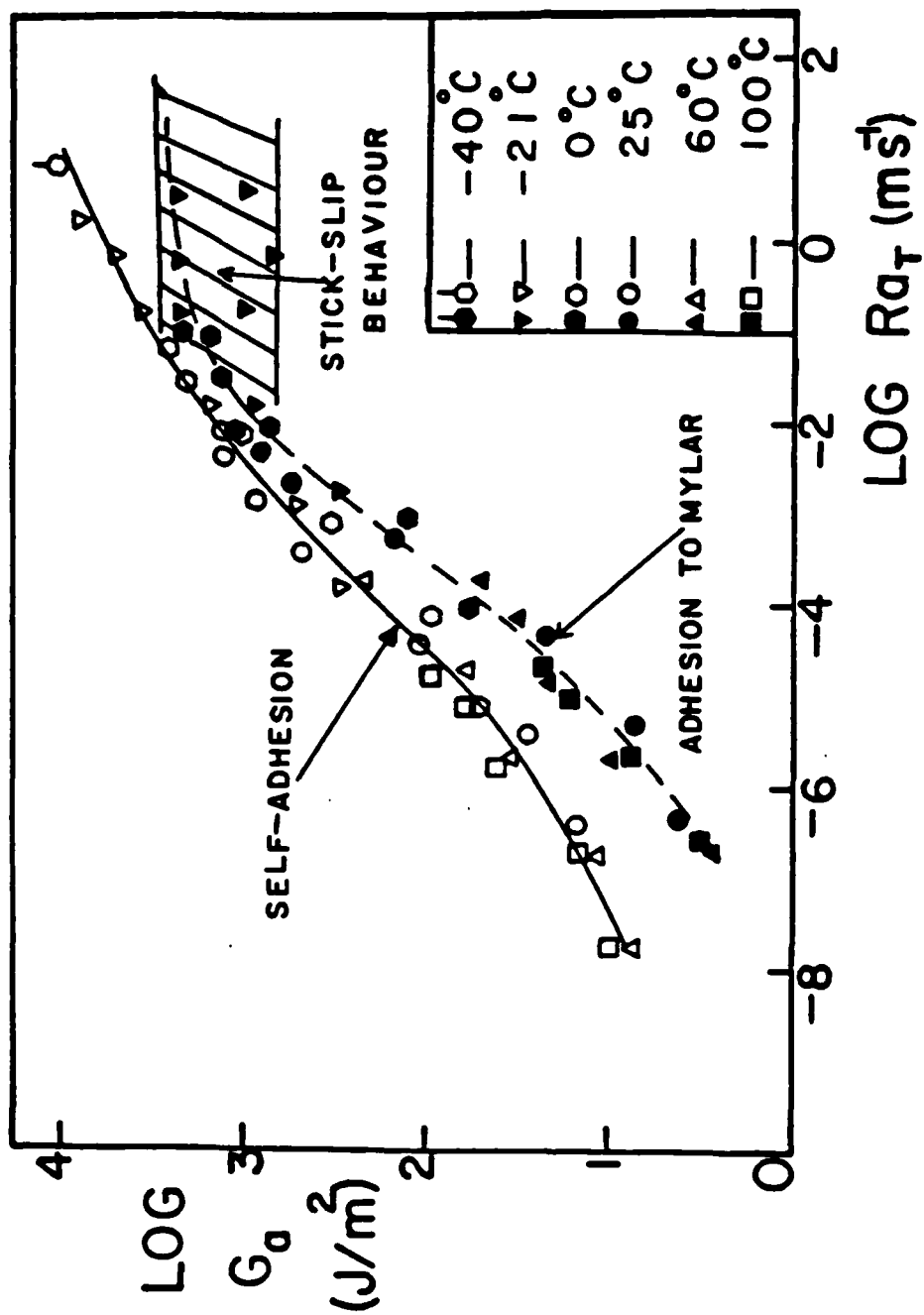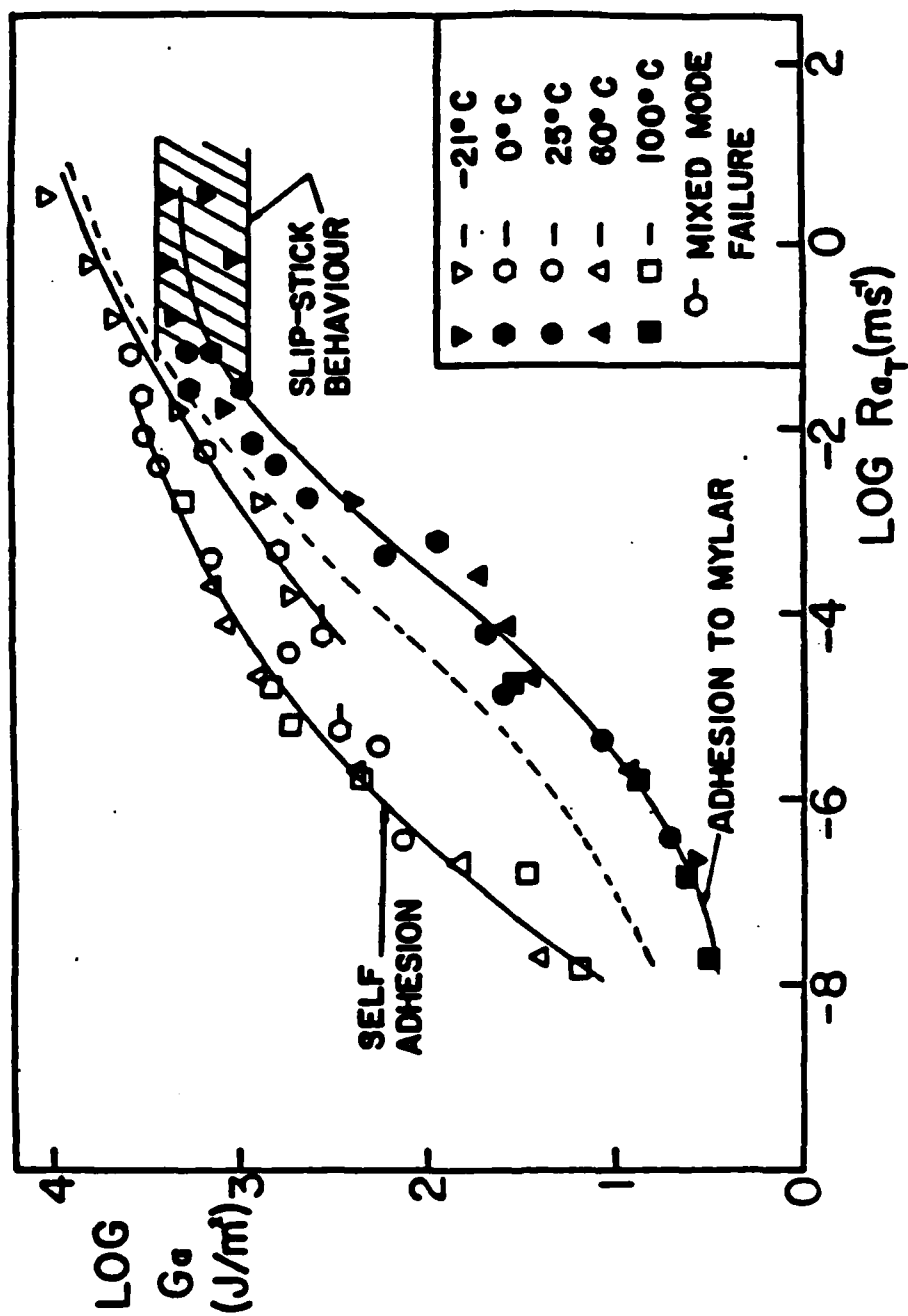
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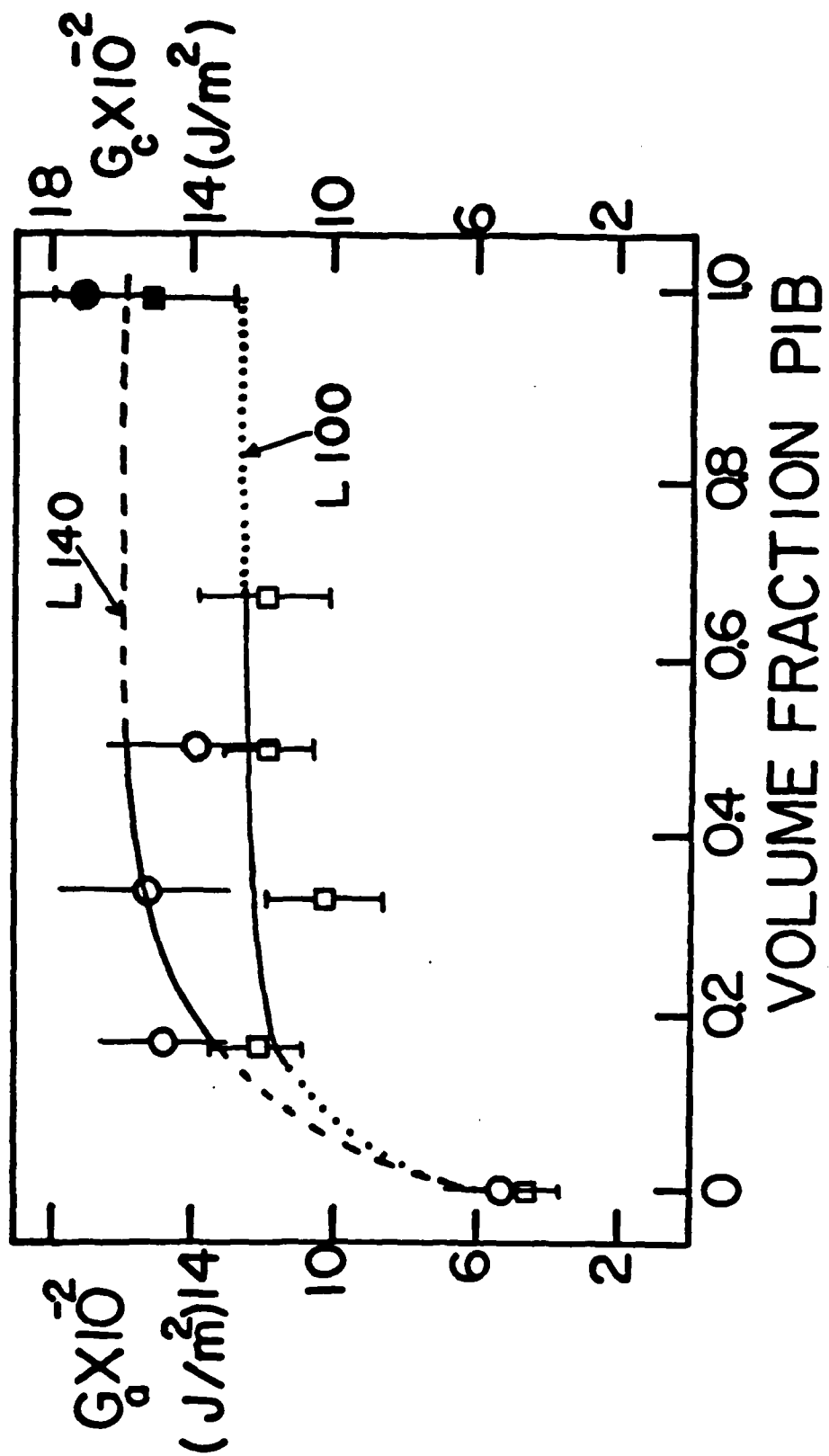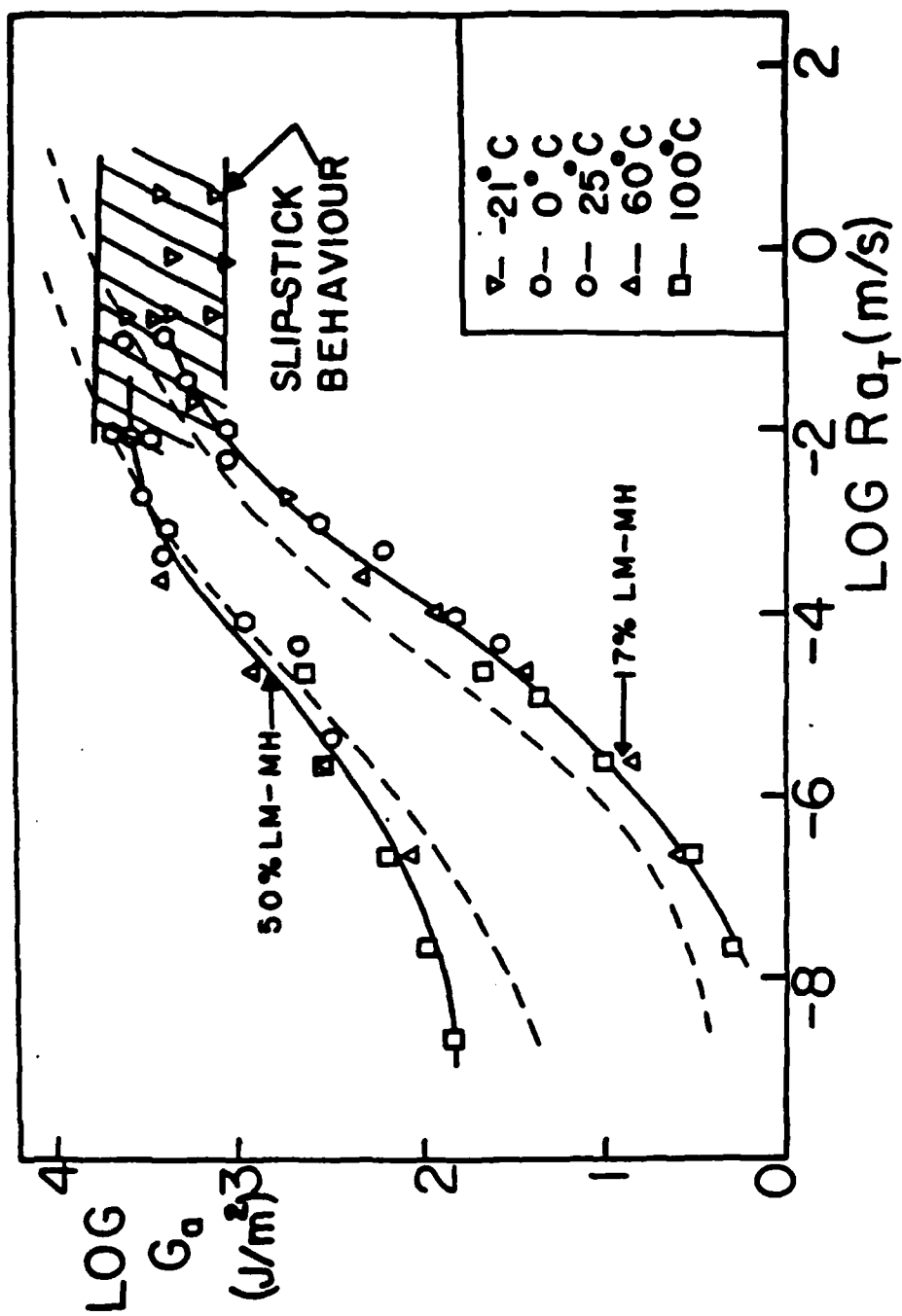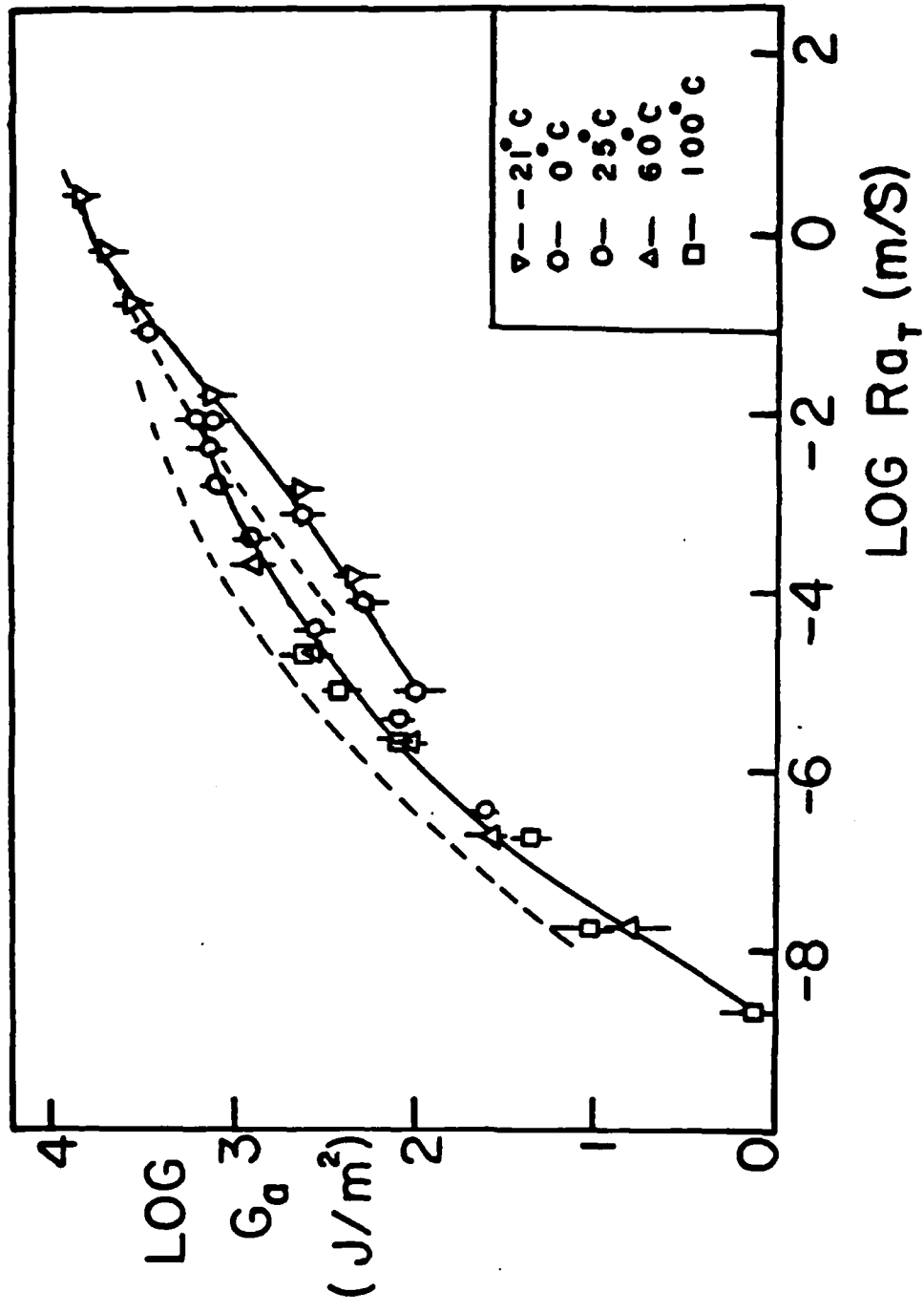
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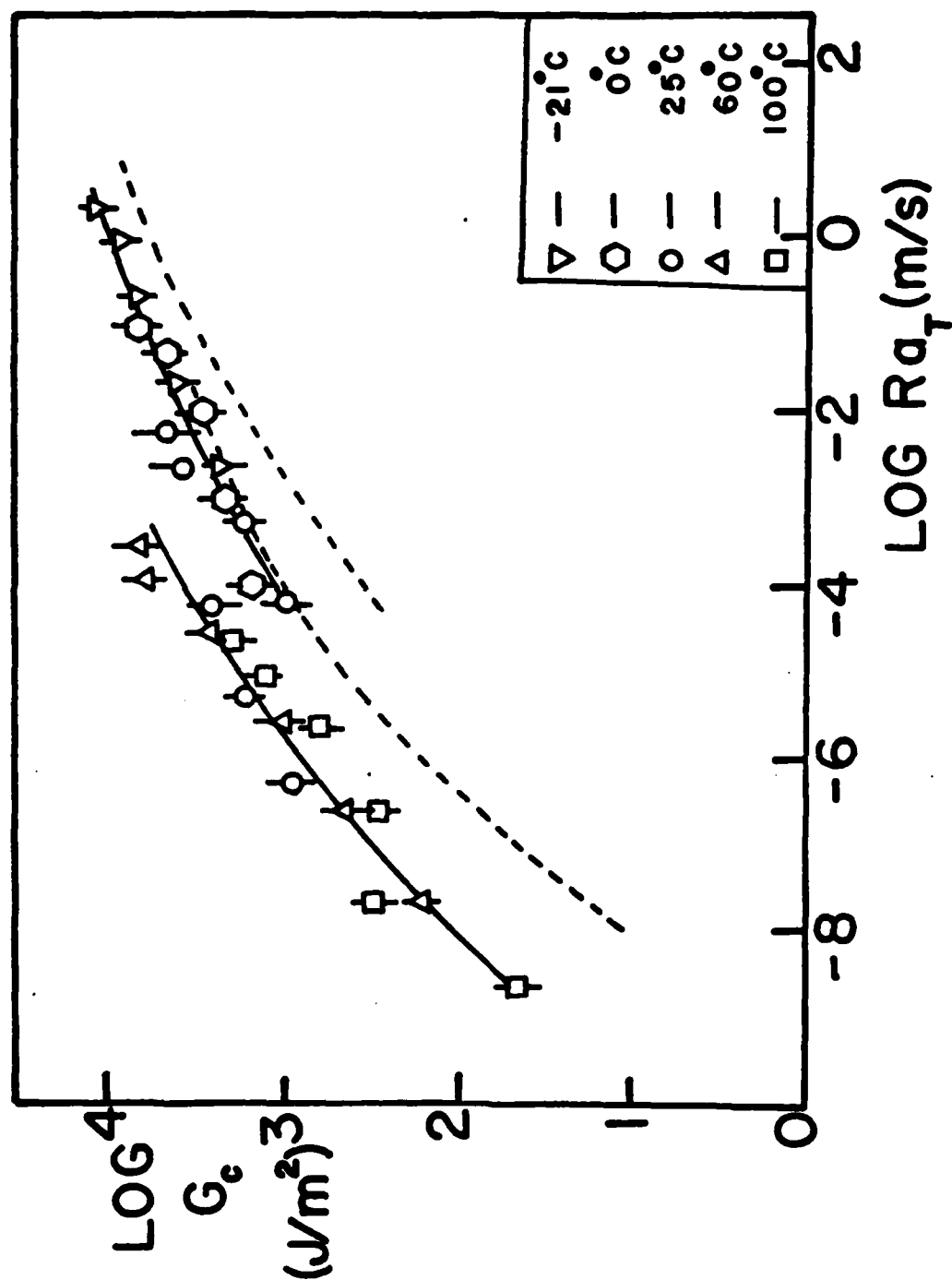
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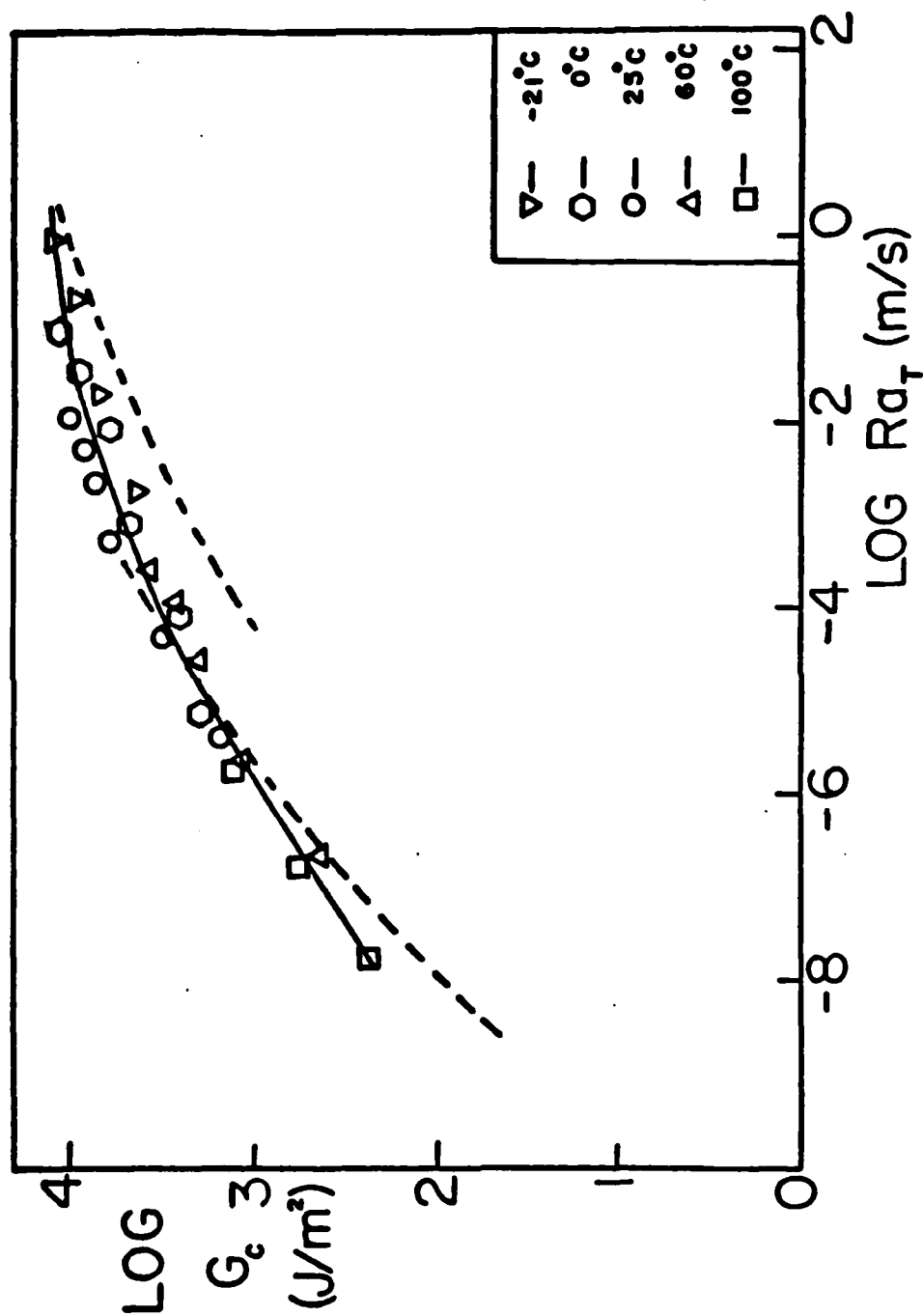Figure 5

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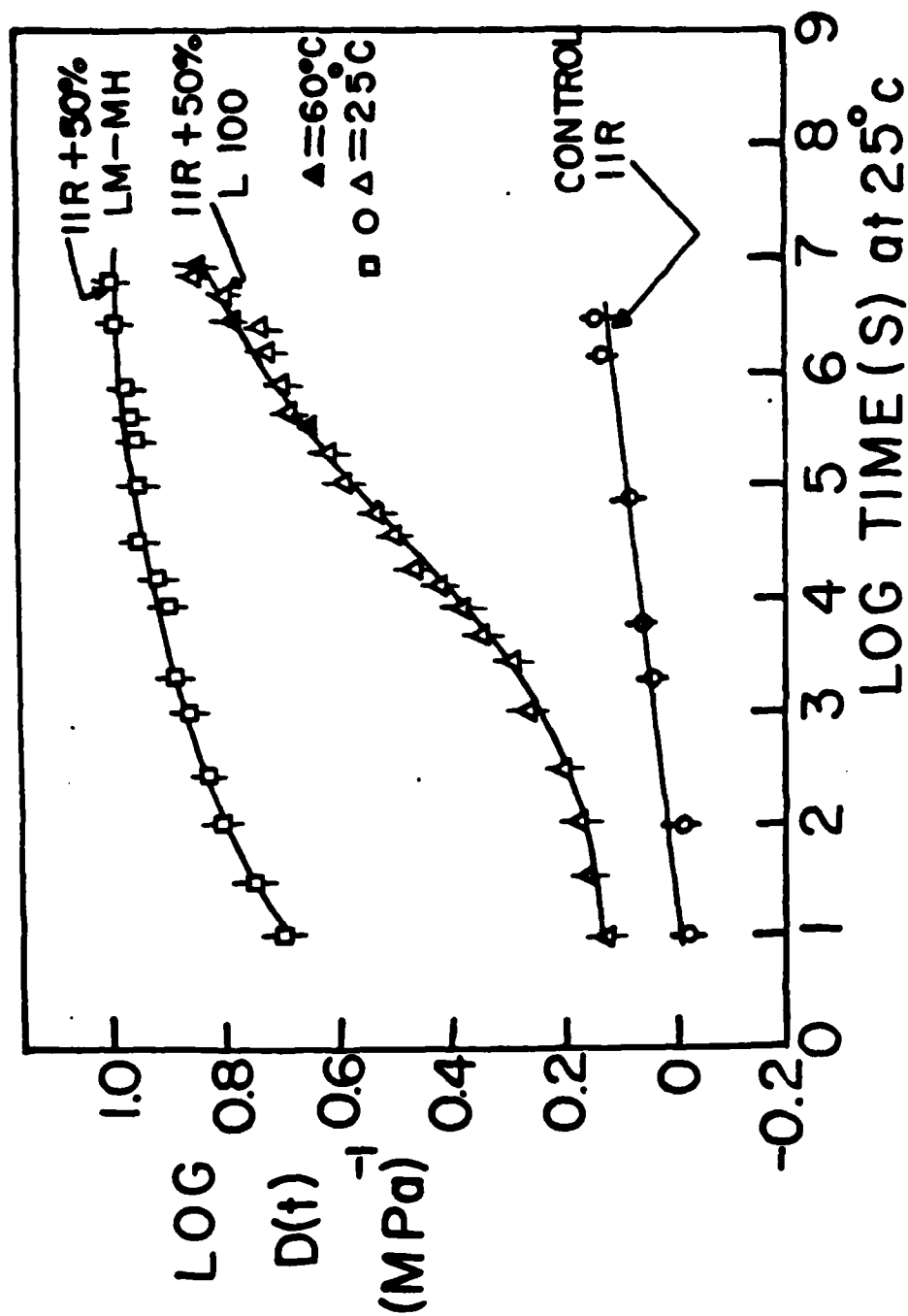
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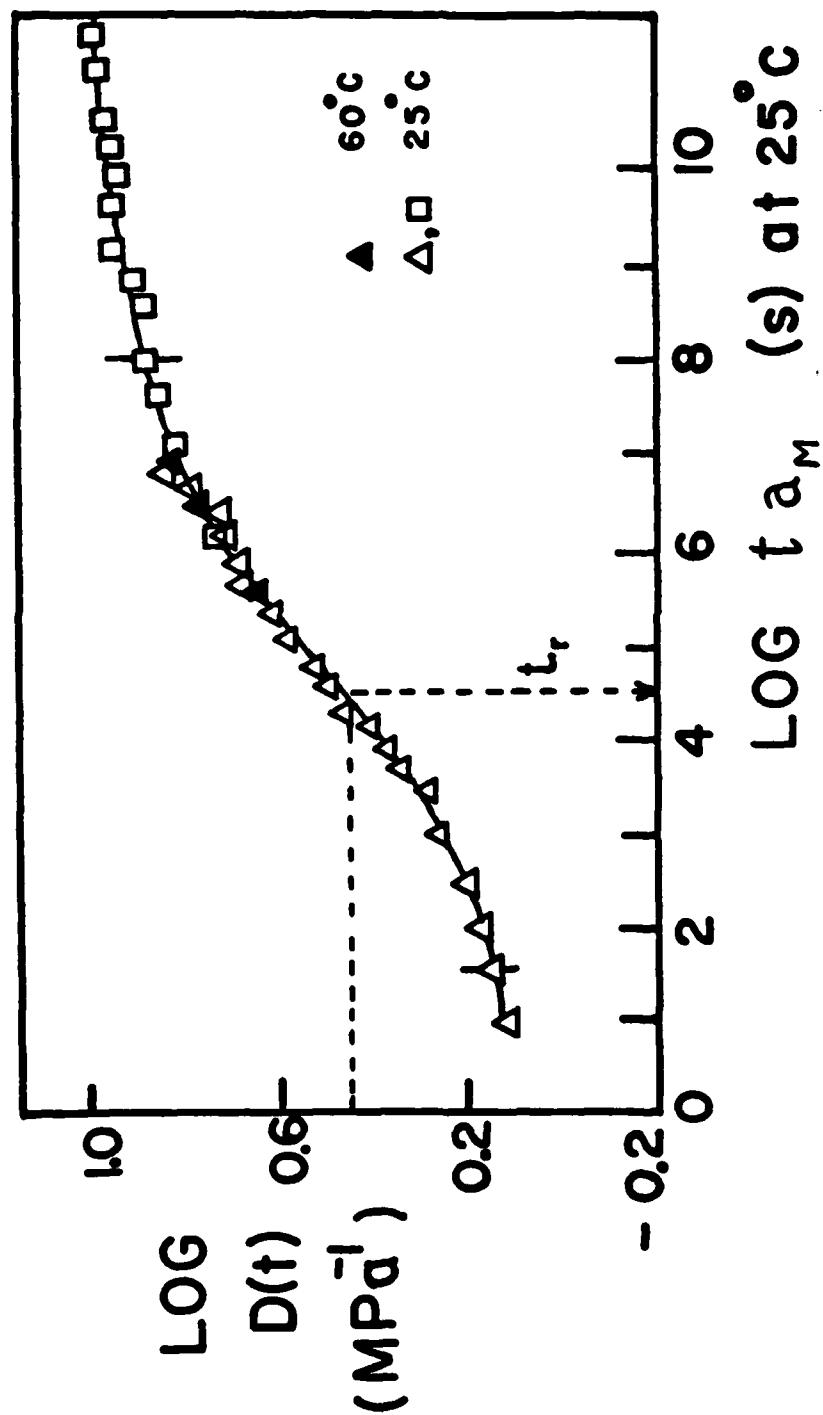
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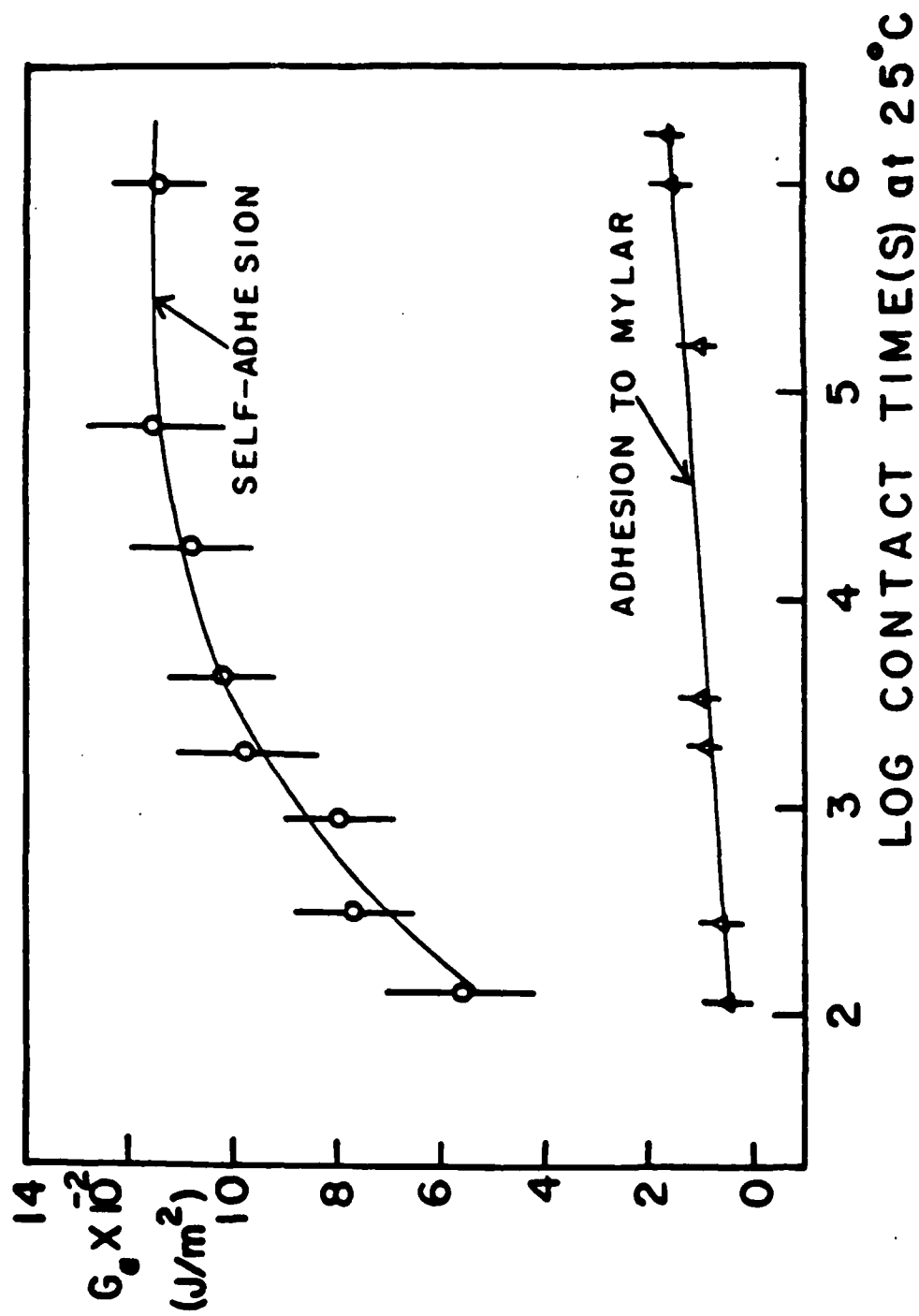
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